Fuel Quality Assurance Research and Development and Impurity Testing in Support of Codes and Standards

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Project # SCS007

Project Goals

1. Hydrogen Contamination Detectors: detect impurities ≥ SAE J2719 levels in **t < 5min**.

A. Offline Analysis : Novel hydration scheme

- Technology Commercialization Fund (TCF) Work
- Develop low-cost components and test
- Obtain independent validation: Gen 1 and 2 HCD

B. Inline Analysis: Anhydrous operation

- Measure Baseline Results/ Test with varying [CO]
- Investigate CO coverage, resistance change
- Improved sensitivity: vary binder, [H_3PO_4], and Pt

Impact

- **Offers an inexpensive method to alert HRS of fuel compliance**
- **Potential to perform uninterrupted inline measurements at HRS**

2. Hydrogen Fuel Quality: SAE/J3219 and ISO

A. SAE-J3219/Technical Information Report (TIR)

- Introduce Standardized Test Matrix/Spreadsheet
- Test MEAs for feasibility before exposure to cleaners

B. International HFQ Efforts (ISO-14687-2)

- Identify area of collaboration & roles of key players
- Establish round robin testing materials/sites

Impact

- **Offer preventive measures for potentially harmful cleaners used at HRS**
- **ISO documents are on 5 year renewal cycles (2022)**

Overview

Timeline and Budget

- Project start date: 10/1/06
- Project end date : 9/30/22

Budget

- Total project funding: $**7,025** K
  - Hydrogen Fuel Quality Standards and Hydrogen Safety Sensor : $3575K (2006-2015)
  - Hydrogen Contaminant Detector (HCD)

    $3,300 K (2013 - Present)

FY21 HCD Funding : $500K

FY21 Fuel Quality Funding: $150K

Barriers

- G. Insufficient Technical Data to Revise Standards
- K. No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

Partners/Collaborators

- **H2Frontier (Burbank, CA)**
- **SKYRE (Formerly Sustainable Innovations)**
- **NREL, Bill Buttner**
- **VI Control Systems of Los Alamos**
- **FORD**
- **HNEI & UConn**
- **International Collaborators:**
  - **JARI**
  - **EU(SINTEF, VTT, CEA)**

Outline

- **Project Goal: Scope and Approach**
- **HCD Development and Deployment**

  Offline HCD Deployment
  - DOE Technology Commercialization Project (TCF)
  - New HCD and Components for Low-Cost System
  - Validation and Verification Testing

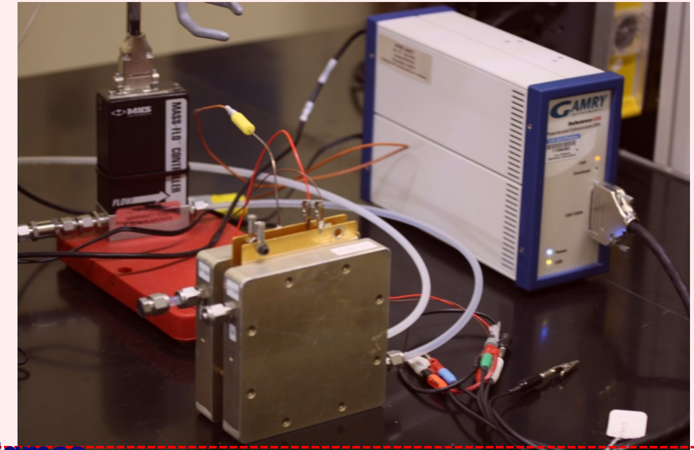
  Inline HCD Development
  - Inline Analysis: PBI based-HCD: Anhydrous Operation
  - Impedance Spectra CO Impacts
  - Cyclic Voltammetry CO Impacts

  Fuel Quality
  - SAE Support
  - International Collaborations
- **Summary/Future Work**

Offline HCD Development Work

- HCD presently requires a Gamry Reference 600^{+} potentiostat to control HCD.
- Laboratory, analytical grade instrumentation system in use.
- ~$17K for a Gamry system plus computer system / Full Echem analysis software package required.
- Portable and compact for essentially a laboratory experiment – used at H2Frontier field test location
- Other expensive components: Fuel Cell Technologies single cell hardware, mass flow controller, and industrial rated control computer

Total laboratory test system cost here ~ $22.5K + computer system.



lab

field

Photos taken at H2F filling station, Burbank CA.

TCF HCD Development Work

Collaborators:

Los Alamos NATIONAL LABORATORY

SKYRE

H2 Frontier Inc
Hydrogen Generation, Storage & Delivery Systems

ONEH2
ZERO EMISSIONS ENERGY

- Design and test a control module and software package to do what the Gamry presently does but at a fraction of the cost.
- Control module must apply proton pumping voltages and clean-up cycles while logging current and HCD temperature.
- Use a current interrupt approach to measure a membrane resistance.
- Accept an alarm point to signal or take action to suspend or actuate valving to isolate filling station storage system from reformer system when H_2 fuel quality falls below spec.
- Work with Skyre Inc. to test 1st and 2nd generation HCD and provide commercialization plan / path forward.
- We selected VI Control Systems of Los Alamos as a design/development partner.
- Continue partnership with H2Frontier/ONEH2 to select filling stations to field test new systems / provide systems design input

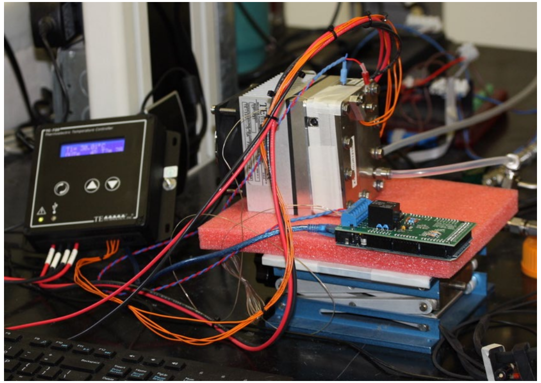
Tech Transfer Activity

New HCD and Components for Low-Cost System

- **Present retail cost, not including labor, recently estimated to be $3215/system.**
- **Compare to previous system field-tested at Burbank H2F which cost $22,500 not including the cost of the required refrigerated instrument cabinet.**

✓Machined Ti HCD plates: $400/set
✓Membrane/GDLs/GDE WE/CE: ~ $50ea
✓Peltier thermal module: $175
✓Peltier controller: $750
✓Machined Al adapter plate: ~ $240ea
✓VI Controls HCD controller: $1500ea
✓Misc: ~$100/unit

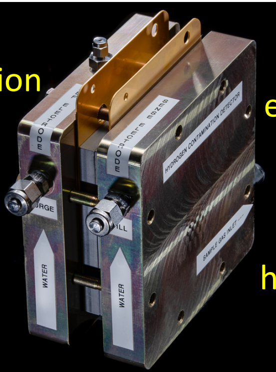
- Relay and MOSFET added for external control of H2Frontier E-stop system to shut down H_2 delivery to storage if CO rises above 200 ppb from methane reformer system. Arduino based system



Gen 2: Peltier thermal module controls temperature for flexible deployment

Gen 1 Field test at Burbank: HCD and Gamry unit were placed inside refrigerated enclosure already onsite.

1st Generation HCD



Uses expensive FCT fuel cell testing hardware.

$22.5K

2nd Generation Prototype HCD and stand-alone controller

Machined Ti endplates & Stainless steel components

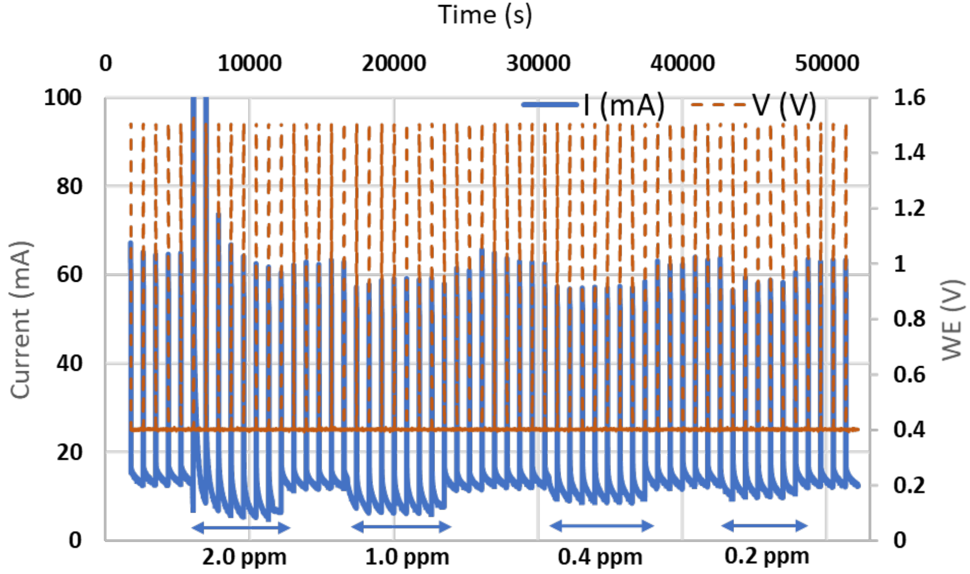
$3.2K

Tech Transfer Activity

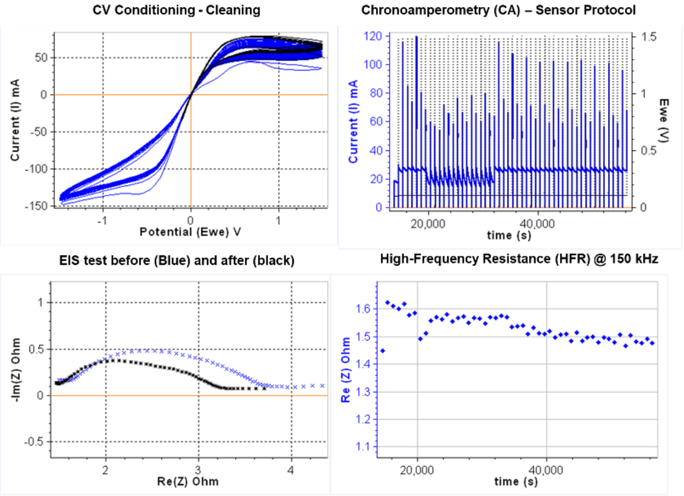
Validation and Verification Testing HCD

- HCD test results provided by Skyre reproduce the performance characteristics and testing results obtained at LANL and at the H2Frontier hydrogen fueling station.
- Low cost (Gen2) HCD performance comparable to Gen1

Results from Skyre (CRADA final report)



2^{nd} Gen HCD performance in 0.2, 0.4,1.0, and 2.0 ppm CO



1^{st} Gen HCD performance in 200ppb CO

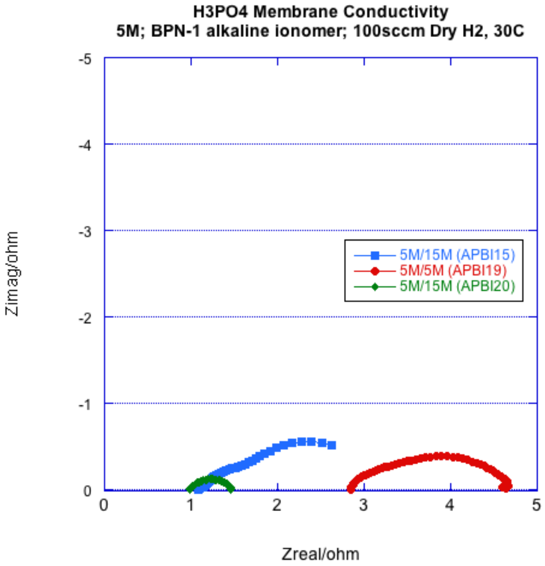
Contaminant Concentration vs. HCD test parameters	Zero-Grade H_2	2 ppm CO in H_2	1 ppm CO in H_2	0.4 ppm CO in H_2	0.2 ppm CO in H_2
Baseline Current (mA)	30	30	25	28	28
Current Upon Contamination (mA)	N/A	12	12	20	22
% of Contamination	0%	60%	52%	29%	21%
Recovery of Baseline	Yes	Yes	Yes	Yes	Yes
Cell Resistance (Ohm)	1.2-1.3	1.5-1.7	1.3-1.5	1.5-1.7	1.4-1.7

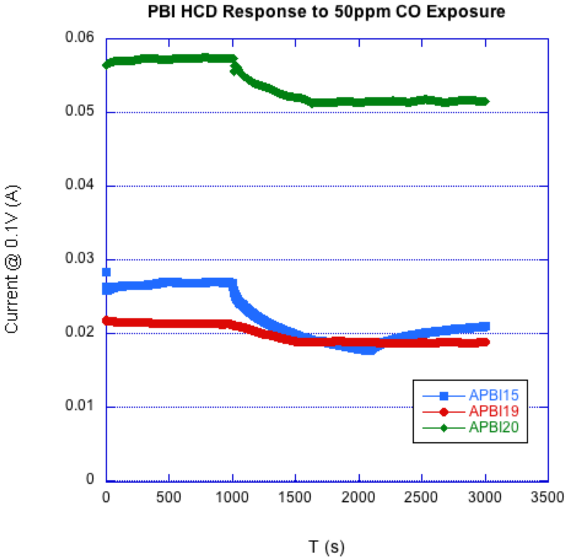
1^{st} Gen HCD performance in 0.2, 0.4,1.0, and 2.0 ppm CO

Tech Transfer Activity

Inline Analysis: PBI based-HCD: Anhydrous Operation

Previous PBI results





- Tunable features:
  - Increasing H_3PO_4 reduces HFR, and improves baseline currents.
  - Decreasing Ionomer in electrode, decreases electrode resistance, and improves baseline currents.
- Responds to higher CO concentrations, our focus is now on improving sensitivity.

New Approach

Previous test setup for offline used:

- H_2 wrap around technique
- Limited characterization

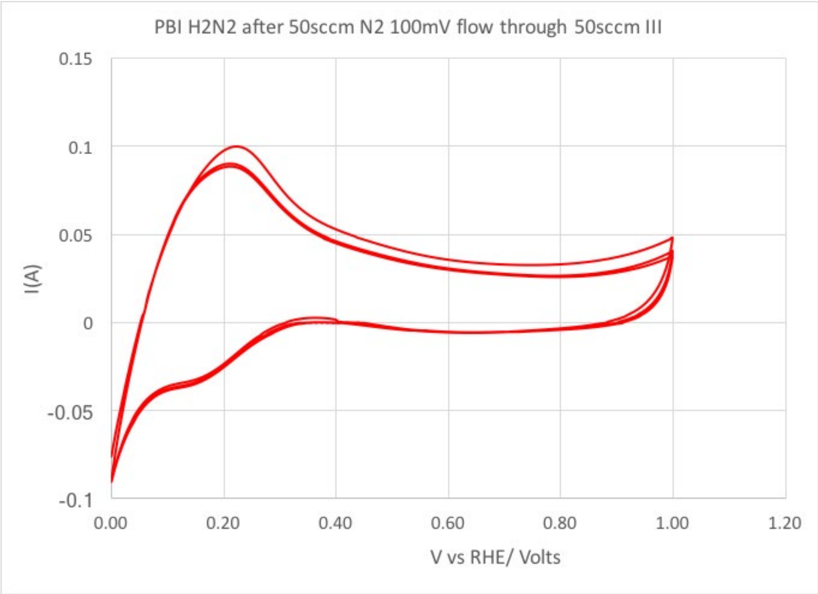
New set-up:

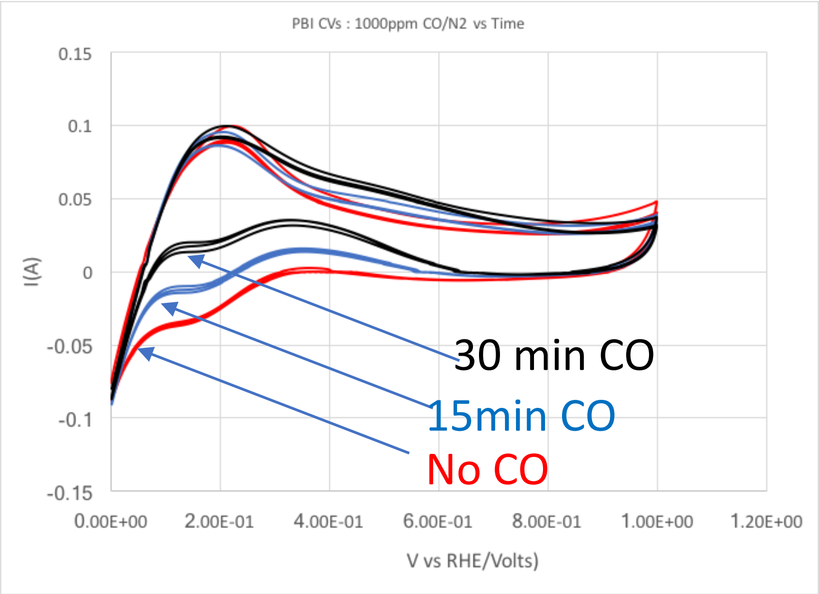
- H_2 dead-ended measurements
- Flow-through measurements
- Expands characterization techniques: CVs, Impedance, Baseline
- Provides a more stable system

Goal

Improve CO sensitivity

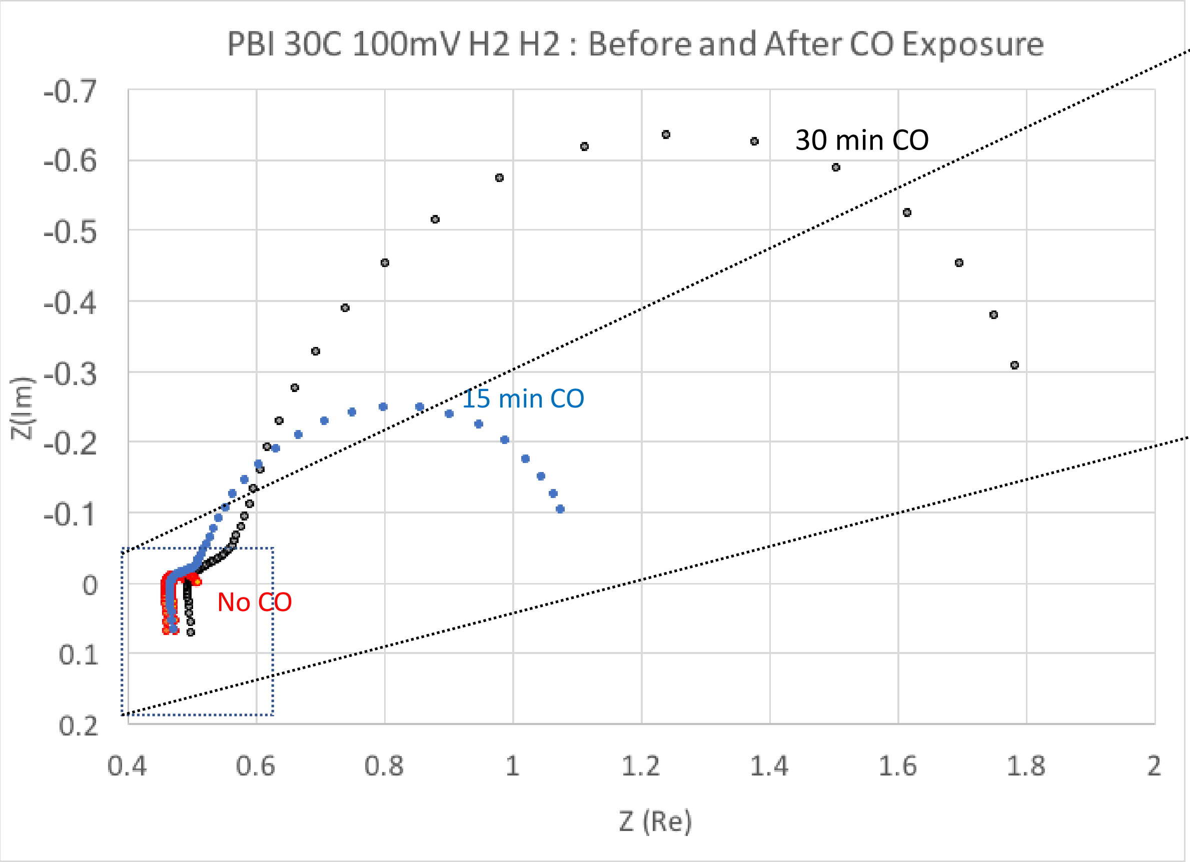
Inline Analysis: Cyclic Voltammetry CO Impacts

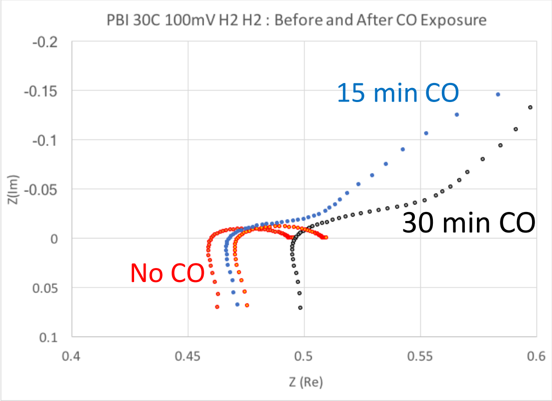




- ➢ CVs were impossible to measure in H_2 wrap around orientation
- ➢ Repeatable CVs were measured with new gas orientation
- ➢ Noticeable suppression in H_2 adsorption region with increasing CO exposure time (dosage)
- ➢ Need to improve response time and sensitivity through electrode design

Inline Analysis: Impedance Spectra CO Impacts





- Increasing charge transfer resistance with increasing CO adsorption
- HFR also increases in the presence of CO
- HFR recovery after CO removal is not complete
- Need to improve response time and sensitivity through electrode design

SAE/J3219 Technical Information Report

- The **purpose** of this TIR is to establish PEMFC testing and characterization methods of chemicals used in HRS during operation/maintenance that could adversely impact PEMFC performance
  - Industry recognized the need due to a lack of testing methods
  - Development of SAE J3219 TIR can provide uniform testing methods
- The **goal** is to bring attention to alternate contaminants(outside of H_2 production techniques).
  - Common chemicals used during HRS operation are refrigerants and lubricants
  - HRS maintenance chemicals typically used are solvent-based cleaning agents and lubricants

SAE/J3219 Development of Detail Spreadsheet

Objectives:

- Describe Materials and Components for Testing
- Establish chemicals for testing to verify testing protocol(s)
- Describe test methods in detail
- Examine cell performance before and after contamination
- Perform Diagnostic tests before and after contamination

	A	B	C	
2	OBJECTIVE: Examine cell performance before and after contamination NOTE: Please complete spreadsheet or submit another input that achieves objective			
3		Testing Lab / LANL	Testing Lab / Uconn	Testi
24				
25	Performance Measurements			
26	BOL Testing (Steady-state or VI)	VI (BOL Polarization Curve)	VI and CC/CV	
27	Test w/Impurities (Steady-state or VI)	VI (Voltage Drop with Time of Exposure)	CC/CV	
28	EOL Testing (Steady-state or VI)	VI (EOL Polarization Curve)	VI and CC/CV (recovery)	
29				
30	VIRs			
31	CC or CV Mode	Constant Current or Constant Voltage	CC is preferred, for very large decays we sometimes revert to CV	
32	Delay time	Time duration at each polarization point		
33	Increasing V/I or two-way VIR curve		Increasing I start at OCV	
34				
35	Discussion/Results			
36	Voltage-loss	Yes		
37	Current-loss	Yes		
38	Tolerant(what's acceptable)	Yes		
39				
40				

Materials & Components Details | Impurity Type | Steady State-Contamination Test | Performance Curves | CVs | EIS

Ready Count: 13

Developed in tandem with **FORD** and valuable input from **UConn**, and **HNEI**. **HNEI** provided a detail report on how to introduce impurities into an operating. Baseline testing of MEAs, underway.

International H2 Fuel Quality Efforts (ISO-14687-2)

Nov 2020: Invitation to collaborate on hydrogen impurity testing received from Japan Automobile Research Institute (Dr. Takahiro Shimizu):

- *"collaborate on hydrogen impurity testing for the next ISO 14687 revision"*
- *"LANL and JARI have been contributing to fuel quality and durability issues for many years, it seems very effective to share the knowledge and experience, and conduct experiments in each country."*
- <u>*"International collaboration between LANL/EU/JARI would also be great."*</u>

Agenda

EU/LANL/JARI meeting on hydrogen quality for fuel cell vehicles

LANL	SINTEF	JARI	Topic	Presenter
6:00	14:00	22:00	Opening of the meeting: introductions and welcome remarks	Hiroaki Tamura / JARI
6:05	14:05	22:05	1) Introduction of each project status for hydrogen quality focusing on fuel cells (*1)	
			• Japan project • EU Metrohyve 2 project • US Project	Yoshiyuki Matsuda / JARI Thor Aarhaug / SINTEF Tommy Rockward / LANL
6:45	14:45	22:45	2) Discussion on future collaboration: hydrogen impurity testing	
			• Toward the revision of ISO 14687 • Technical issues (Fuel cell testing, Gas analysis, etc) (*2)	All the participants
7:00	15:00	23:00	End of the meeting	Hiroaki Tamura / JARI

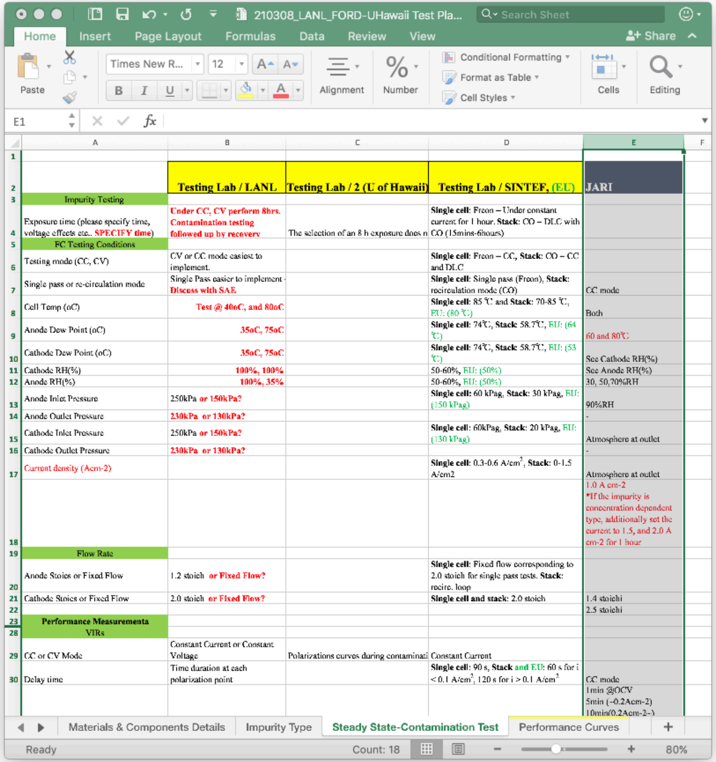
(*1) 10-13 min presentation includes discussion. Prepare presentation materials if necessary.
(*2) Please let us know if there are any specific items to add.

JARI 3

Collaboration began in Dec 2020

International HFQ Efforts (ISO-14687-2)

- Dec 10, 2020: Virtual Kick-off Meeting Held: LANL/EU/JARI
  - Introductions/Current efforts/Interests
- Feb 17, 2020: Developing a Harmonized Approach:
  - Share the each evaluation methods and its concept
  - Harmonization of the evaluation method
  - Round-robin test of single cell- harmonized evaluation method
  - Apply the evaluation method in each institute, data discuss
- Next Meeting: April 26, 2021
  - Establish timeline of activities thru 2022



	Testing Lab / LANL	Testing Lab / 2 (U of Hawaii)	Testing Lab / SINTEF, (EU)	JARI
Impurity Testing				
Exposure time (please specify time, voltage effects etc.. SPECIFY time)	Under CC, CV perform 8hrs. Contamination testing followed up by recovery	The selection of an 8 h exposure does n	Single cell: Freon – Under constant current for 1 hour. Stack: CO – DLC with CO (15mins-6hours)	
FC Testing Conditions				
Testing mode (CC, CV)	CV or CC mode easiest to implement.		Single cell: Freon – CC, Stack: CO – CC and DLC	
Single pass or re-circulation mode	Single Pass easier to implement - Discuss with SAE		Single cell: Single pass (Freon), Stack: recirculation mode (CO)	CC mode
Cell Temp (oC)	Test @ 40oC, and 80oC		Single cell: 85 ℃ and Stack: 70-85 ℃, EU: (80 ℃)	Both
Anode Dew Point (oC)	35oC, 75oC		Single cell: 74℃, Stack 58.7℃, EU: (64 ℃)	60 and 80℃
Cathode Dew Point (oC)	35oC, 75oC		Single cell: 74℃, Stack 58.7℃, EU: (53 ℃)	See Cathode RH(%)
Cathode RH(%)	100%, 100%		50-60%, EU: (50%)	See Anode RH(%)
Anode RH(%)	100%, 35%		50-60%, EU: (50%)	30, 50,70%RH
Anode Inlet Pressure	250kPa or 150kPa?		Single cell: 60 kPag, Stack: 30 kPag, EU: (150 kPag)	90%RH
Anode Outlet Pressure	230kPa or 130kPa?			-
Cathode Inlet Pressure	250kPa or 150kPa?		Single cell: 60kPag, Stack: 20 kPag, EU: (130 kPag)	Atmosphere at outlet
Cathode Outlet Pressure	230kPa or 130kPa?			-
Current density (Acm-2)			Single cell: 0.3-0.6 A/cm^2, Stack: 0-1.5 A/cm2	Atmosphere at outlet
				1.0 A cm-2 *If the impurity is concentration dependent type, additionally set the current to 1.5, and 2.0 A cm-2 for 1 hour
Flow Rate				
Anode Stoics or Fixed Flow	1.2 stoich or Fixed Flow?		Single cell: Fixed flow corresponding to 2.0 stoich for single pass tests. Stack: recirc. loop	
Cathode Stoics or Fixed Flow	2.0 stoich or Fixed Flow?		Single cell and stack: 2.0 stoich	1.4 stoichi
				2.5 stoichi
Performance Measurementa				
VIRs				
CC or CV Mode	Constant Current or Constant Voltage	Polarizations curves during contaminati	Constant Current	
Delay time	Time duration at each polarization point		Single cell: 90 s, Stack and EU: 60 s for i < 0.1 A/cm^2, 120 s for i > 0.1 A/cm^2	CC mode
				1min @OCV 5min (-0.2Acm-2) 10min(0.2Acm-2-)

Received additional input from our international collaborators.

Milestones and Progress

Milestone Name/Description	End Date	Status
Title: Low cost Nafion-based HCD **Milestone: Demonstrate the ability of a low-cost Nafion-based Hydrogen contaminant detector to detect CO at or below the SAE J2719 level of 200ppb.**	12/31/2020	100% Complete
Title: Electrode development for PBI-based HCD **Milestone: Complete evaluation of 4 different electrode compositions in a PBI based hydrogen contaminant detector and report on their sensitivity to CO at 2 different ionomer and Pt loadings.**	3/31/2021	100% Complete
Title: Fuel Quality Research **Milestone: Finalize standard test protocol for impurity testing, and report on the impact of 3 different impurities hydrogen fuel impurities on fuel cell performance.**	6/30/2021	50% Complete. On track.
Title: PBI-based HCD development **Milestone: Finalize PBI-based hydrogen contaminant detector design with ability to detect < 200ppb of CO in a dry H2 stream. Demonstrate stable (< ± 10% baseline drift) baseline over a period of 1 week of continuous operation, with > 20% change in current in response to 200ppb CO.**	9/30/2021	25% Complete. Ontrack.

All milestones are on track to be completed

Future Work: HCD

- New Field Testing opportunity (Spring 2021) – extend partnership with H2Frontier beyond experimental system fielded at the H2F Burbank Station in 2018-2019
- Automated "Turn-key" HCD system to be installed at Shell Hydrogen Station in Torrance California. Partnership with ONEH2, Shell, and LANL
- Skyre pursuing commercialization opportunity
- HCD system will continuously monitor product hydrogen leaving steam-methane-reformer and PSA system and before compression to the station storage tanks
- HCD will automatically suspend storage of the hydrogen if the HCD controller detects current falling below calibrated threshold value
- Improve sensitivity of PBI based system to be comparable to the Gen1 and Gen2 Nafion® based system
- Adapt PBI based system for operation under varying pressure and temperature conditions

"Any proposed future work is subject to change based on funding levels."

Future Work: SAE J-3219 /ISO 14687-2

- Complete baseline measurements to validate MEAs
- Test experimental setup to introduce liquid impurities
- Agree upon a set of chemical agents to study
- Evaluate multiple Membrane electrode assemblies (MEAs) to validate testing system
- Report results to SAE
- Support adoption of TIR
- Continue International Collaborations:
- Support JARI efforts at revising ISO standard
- Share evaluation methods/Harmonization of the evaluation method
- Participate in international round robin testing
- Initiate fuel impurity testing amongst the collaborators and disseminate results

"Any proposed future work is subject to change based on funding levels."

Summary

➢ HCD Development and Deployment

Offline HCD Deployment

- ➢ DOE Technology Commercialization Project (TCF) successfully completed (March 2021)
- ➢ New HCD: Gen 2 cost significantly reduced
- ➢ V&V Testing: Skyre was able to reproduce the performance characteristics and testing results obtained at LANL and at the H2Frontier hydrogen fueling station

Inline HCD Development

- ➢ New approach very promising, allowing for more characterization/better stability
- ➢ Impedance Spectra CO Impacts: Charge transfer and HFR increases observed
- ➢ Cyclic Voltammetry CO Impacts: Adsorption region severely reduced

➢ Fuel Quality

SAE J3219 TIR:

- ➢ Detailed spreadsheet developed with valuable input from collaborators
- ➢ MEA testing underway

International Collaborations:

- ➢ Identified key participants
- ➢ Coordination meetings established/collaborations initiated
- ➢ Developed a timeline of activities until ISO 14687-2 revision year (2022)

Acknowledgements

- Our funding source:
  - Laura Hill (Technology Manager)
- Collaborators:
  - H2Frontier (Burbank, CA)
  - SKYRE (Formerly Sustainable Innovations)
  - NREL, Bill Buttner
  - VI Control Systems of Los Alamos
  - FORD
  - HNEI & UConn
  - JARI
  - EU(SINTEF, VTT, CEA)
- And the Audience!!!

Thank you

Additional Slides

Inline Analysis: Baseline CO Impacts

Analyzer PBI	Loading (2.275 cm2 area)	H3PO4 Membrane	GDE/GDE - H3PO4	BPN-1 Alk. Ionomer Sensor Electrode	HFR (Ohm)	Baseline Current	100 PPM CO Current	50 PPM CO Current	10 PPM CO Current	1 PPM CO Current
APBI23	0.035 mg Pt/cm2 - 0.3 mg PtRu/cm2	15M	30AA/30AA - 15M	1.0 mg total dry	0.23 - 0.3	350.3 uA	178.6 uA	n/a	no response	n/a
APBI24	0.038 mg Pt/cm2 - 0.25 mg PtRu/cm2	15M	30AA/30AA - none	0.08 mg total dry	0.27 - 0.5	Bline	519 uA (Bline) / 90.07 uA	n/a	n/a	586 uA (Bline) / 455 uA
APBI25	0.15 mg Pt/cm2 - 0.2 mg PtRu/cm2	10M	29BC/30AA - 10M	0.304 mg total dry	0.9 - 1.0	43.62 mA	n/a	33.09 mA	n/a	no response
APBI26	0.15 mg Pt/cm2 - 0.25 mg PtRu/cm2	10M	29BC/39AA - 10M	0.157 mg total dry	1.2 - 18	Bline	n/a	65.62 mA (Bline)/ 46.80 mA	57.24 mA (Bline)/ 39.98 mA	65.77 mA (Bline)/ 59.47mA

- Evaluated multiple PBI cells to develop pathway to electrode optimization
- Lower Pt loading (0.05 mg/cm^2) and low ionomer loading (< 0.1 mg total dry) hold promise

Working data/ will take a close look to see how responsive the current was…